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Counterintuitive effects of isotopic doping on the phase diagram of H₂-HD-D₂ molecular alloy

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Molecular hydrogen forms the archetypical quantum solid. Its quantum nature is revealed by behavior which is classically impossible, and by very strong isotope effects(1). Isotope effects between H₂, D₂ and HD molecules come from mass difference, and the different quantum exchange effects: fermionic H₂ molecules have antisymmetric wavefunctions, whilst bosonic D₂ molecules have symmetric wavefunctions and HD molecules have no exchange symmetry. To investigate how the phase diagram depends on quantum-nuclear effects, we use high pressure and low temperature *in-situ* Raman spectroscopy to map out the phase diagrams of H₂-HD-D₂ with various isotope concentrations over a wide *P-T* range. We find that mixtures of H₂, HD and D₂ behave as an isotopic molecular alloy (ideal solution), and exhibit symmetry-breaking phase transitions between phases I-II and III. Surprisingly, all transitions occur at higher pressures for the alloys than either pure H₂ or D₂ (2). This runs counter to any quantum effects based on isotope mass, but can be explained by quantum trapping of high kinetic energy states by the exchange interaction.

hydrogen | high pressure | isotope effects | phase diagram

Hydrogen and deuterium have unique and distinctive properties which set them aside from the rest of the periodic table. Hydrogen has the lowest nuclear mass, and H₂:D₂ has the highest isotope mass ratio of any element 1:2. Consequently, quantum effects such as zero-point energy are both large and different for the two isotopes. This energy, combined with the effects of exchange symmetry, via the *para-ortho* distinction, results in fascinating behaviour at low temperatures.

It is believed that the molecular hydrogens form the same series of phases if pressurised and/or cooled, although with measurably different phase boundaries. There are five experimentally described solid molecular phases in the pure isotopes (2–12). In a qualitative description (13), phase I adopts a hexagonal close-packed arrangement of rotating molecules. Rotation at very low temperature is only possible due to quantum nuclear effects for which the rotational ground state has no zero-point energy. Phases II and III are "typical" molecular phases (2, 8), where symmetry-breaking arises from quadrupole-quadrupole interactions (phase II(14)) or efficient packing of elongated molecules (phase III(13)). Phases IV and V possess mixed molecular states with both strongly-bound rotating and weakly-bound molecules (4, 5, 15). The phase I(II)→III transition is density driven, resulting in a close to vertical phase line (quasi-isobaric) separating the two phases (2, 16, 17). Conversely, the I→II and III→IV(V) transformations are mostly temperature (entropy) driven, resulting in a flatter phase line (quasi-isothermal) separating the partially-ordered phase II from the rotor phase I, and the

mixed-molecular phases IV(V) from phase III (4, 18). The situation is further complicated by the *para-ortho* distinction: due to the exchange symmetry, *o*-H₂ is unable to be in the *J* = 0 molecular rotational ground state. This means that phase I of *o*-H₂ has higher energy than phase I of *p*-H₂, and therefore *o*-H₂ transforms more easily to phase II than *p*-H₂.

Hydrogen deuteride has been studied less than the pure isotopes, and its spectroscopy is complicated by the localisation of the vibrational modes. Pure HD was claimed to have a phase II with an unusual "re-entrant" phase line at low temperatures (19, 20), and on further compression above ~160 GPa, to transform to phase III (21). Recently, using Raman spectroscopy, phase IV was found in H₂, HD and D₂ mixtures at 300 K(1). A subsequent infra-red study of pure HD claimed to observe dissociation at 77 K, and at pressures above 160 GPa, claimed the existence of two novel phases (HD-IV* and HD-PRE)(22), which do not exist in pure isotopes.

Recently, we reported the behaviour of the pure isotopes at low temperatures up to pressures of 210 GPa, characterising the phase transition criteria between phases I, II and III. These measurements suggested the existence of a phase II' in D₂ which is not observed in H₂ (2, 23). We speculated that its presence is related to the lower zero-point energy of D₂ compared to H₂ and more complex rotational movement (2). The presence of both isotopes, H and D, makes only a subtle difference to the electronic structure, but the disorder can fundamentally change vibrational properties from its pure

Significance Statement

When hydrogen and deuterium are mixed they form H₂+HD+D₂ mixtures at very low pressures and room temperature. We show that at high pressures and low temperatures these mixtures behave as an isotopic molecular alloy (ideal solution), exhibit symmetry-breaking phase transitions between phases I, II and III and shift to higher pressures the transformations to phases II and III as compared to pure isotopes. This runs counter to any quantum effects based on isotope mass, but can be explained by quantum trapping of high kinetic energy states by the exchange interaction.

X.D.L. performed the experiments, contributed to the analysis and discussion of results and wrote the paper. P.D.S. and R.T.S. conducted the experiments, contributed to the analysis and discussion of results and wrote the paper. H.C.Z., W.X. and J.B. conducted the experiments. G.J.A. contributed to the analysis and discussion of results and wrote the paper. H.K.M. contributed to the discussion of results and provided the materials/analysis tools. E.G. designed the research, contributed to the analysis and discussion of results, wrote the paper and contributed the materials/analysis tools.

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counterparts. In an HD molecule, the nuclei are distinguishable, so there is no *ortho-para* distinction, allowing all angular momentum states ($J = 0, 1, 2, \dots$). Additionally, HD molecules possess a small permanent dipole moment (5.85×10^{-4} D) as well as the centre of mass being off-centre. All of these, together with the random distribution of the isotopes in the solid (1), might significantly affect the formation of phase II. Such effects raise important questions about how isotopic mixtures behave; how do the quantum effects due to mass and to *ortho-para* symmetry compete; would the isotopes separate, and if not would the isotopic disorder play any role in packing of the molecules; could new phases exist; will each species break symmetry at the same P - T conditions and how might isotopic doping alter the phase boundary?

Here, we study compressed hydrogen-deuterium mixtures at low temperatures. Remarkably, we find that the mixtures have a higher transformation pressure (equivalently, lower temperatures) to phases II and III than either H_2 and D_2 . For example at 20 K, the mixtures enter phase II above 65 GPa and phase III above 170 GPa depending on concentration, while for n - D_2 (H_2) these pressures are ~ 20 (~ 60 GPa (2, 24)) for phase II and 165 (160) GPa for phase III (2). Since HD has mass intermediate between H_2 and D_2 , this cannot be due to mass effects alone.

We studied three concentrations of mixtures H:D=40:60 (D_2 -rich), H:D=50:50 and H:D=75:25 (H_2 -rich). Upon loading the mixtures of H_2 and D_2 at 0.2 GPa, we observe the formation of HD within minutes at 300 K. Assuming the reaction $H_2 + D_2 \leftrightarrow HD$ is completely reversible, the following molecular isotopic alloys are formed from the initial concentrations, 40:60 - $(H_2)_{0.16}(HD)_{0.48}(D_2)_{0.36}$, 50:50 - $(H_2)_{0.25}(HD)_{0.5}(D_2)_{0.25}$ and 75:25 - $(H_2)_{0.56}(HD)_{0.38}(D_2)_{0.06}$ reflecting the overall intensity distribution at low pressures (1) (see SI Appendix, Figs. S2-S3). This results in mixtures that have comparable HD concentrations, varying by a maximum of 20%, whereas the D_2 concentration varies from 6-36%.

Measurements were conducted through both isobaric cooling/heating cycles and isothermal compressions at low temperature (see Fig. 1). We identify the phase changes using standard phase transformation criteria (2), namely the appearance of new, sharp, low-frequency excitations and changes in the pressure/temperature dependence of the vibron frequencies.

Fig. 2 shows a representative temperature scan of the 75:25 mixture at 116 GPa. As the temperature is decreased below 75 K, both criteria are clearly observed in the Raman spectra: the appearance of the new peaks (left panel) and the change in temperature dependence of the vibrational frequencies (right panel). It is significant that the changes in the frequencies of the H-H and H-D vibrons vs. temperature happen simultaneously and have the same shapes as observed in pure D_2 and H_2 at similar pressures (2). At this particular concentration, we also observe noticeable asymmetric broadening of all stretching modes, with the D-D appearing as a doublet in phase I (Fig. 2, central panel) and on the transition to phase II, a 3^{rd} peak can be resolved at the same temperature as the change of vibrational frequency temperature dependency of the H-H and H-D modes (see Fig. 2 and SI Appendix Figs. S4-S5). The asymmetric broadening of the Raman modes in mixtures at 300 K was reported before, but no splitting was observed (1). The splitting (less resolved but still present

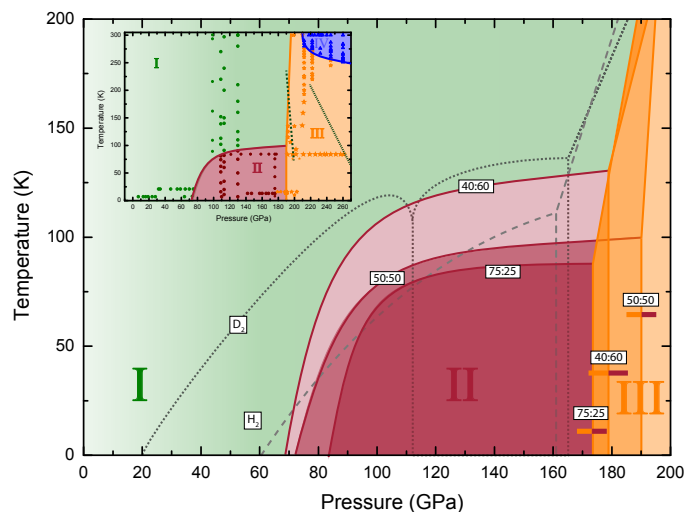


Fig. 1. Proposed low temperature phase diagrams of three representative H_2 - D_2 mixtures (H_2 : D_2 ratios of 75:25=3:1, 50:50=1:1 and 40:60=2:3). Phase-I is shown in green, phase-II in red and phase-III in orange. Different shades of colour in phase-II and phase-III represent a different mixture concentration. The grey dashed lines represent the phase boundaries of the pure isotopes taken from Ref. (2). Inset: Extended phase diagram of the individual 50:50 mixture, showing collected data points on isothermal compression and isobaric cooling cycles. Phase IV is shown in blue. Green lines represent previously proposed boundaries from Ref. (22). We see no evidence for re-entrant phase boundaries down to 13 K.

for H-D and H-H modes) could be explained by the mode localisation arising from the different atomic environment (25). In all the three concentrations studied, changes to H_2 , D_2 or HD modes happen simultaneously, showing that the mixtures behave as a molecular alloy (see SI Appendix, Figs. S4-S6). It is interesting to note that we have never observed spectra similar to those of phase-II in pure HD (19).

Figs. 3 and 4 show the evolution of the low frequency (librons) and vibrational parts (vibrons) of the Raman spectrum of three mixtures during the isothermal compression in the 7 - 200 GPa pressure regime. At low pressures, *i.e.* 7 to 20 GPa, the rotational part of the spectra could be described as the linear superposition of three independent isotopic molecules, although the rotational modes of HD are considerably broader than those of D_2 and H_2 (see SI Appendix, Fig. S3 and also Ref. (1)). We propose that the broadening can be understood by the offset of the centre of mass: as the HD molecule rotates, its charge density "wobbles" much more than H_2 , facilitating collisions with adjacent molecules. This reduces the rotational mode lifetime and increases the HD rotor line-width.

The vibrational modes can be assigned to 3 types of molecules, however their frequencies are all higher in mixtures than in the pure isotopes (see SI Appendix, Fig. S12). This is due to resonant coupling between the vibrations on identical molecules. In mixtures, most neighbours are of a different species, hence there is vibrational decoupling and the modes are more localised. Coupling has two effects: it shifts the mean frequency downwards and creates dispersion: since the Raman active mode has typically the lowest frequency in the phonon band, the dispersion lowers the Raman frequency further. By contrast, the IR active modes are nearer the top of the band, so in IR the two effects tend to cancel out. In fact, the Raman vibrational frequencies of H-H, H-D and D-D modes in mixtures are located at the range between Raman

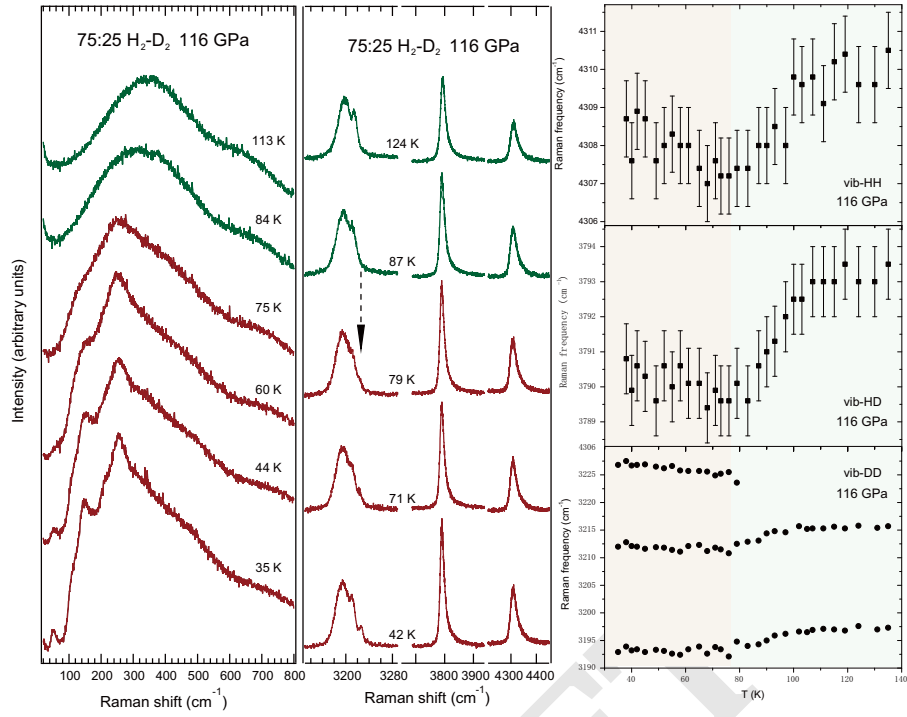


Fig. 2. Left Panel and Middle Panel: Representative rotational, librational and vibrational Raman spectra of a 75:25 H₂-D₂ mixture as a function of temperature at 116 GPa. Arrow indicates of the appearance of a new vibrational mode at the transition to phase II. The D-D peak is *narrower* than the others: note the change in scale on the x-axis. Right Panel: Vibron frequencies of H-H (top), H-D (middle) and D-D (bottom) as a function of temperature at 116 GPa for the same mixture concentration. The error bars are the fitting error of the position of vibron frequencies. Colours indicate phase-I (green) and phase-II (red).

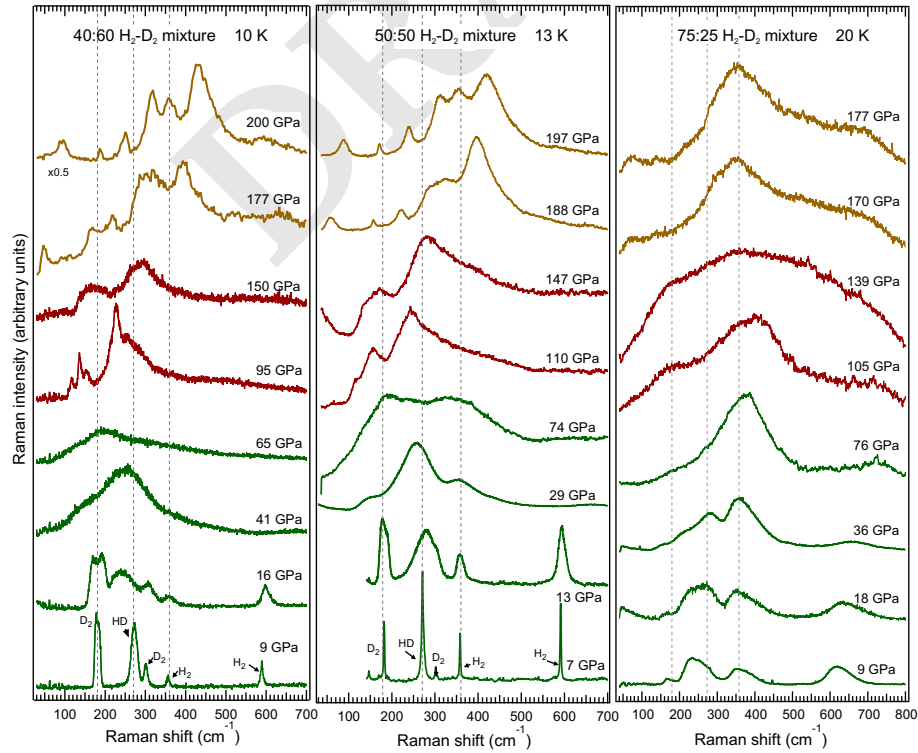


Fig. 3. Representative low frequency Raman spectra of 40:60, 50:50 and 75:25 H₂-D₂ mixtures as a function of pressure at 10 K, 13 K and 20 K respectively. Colours indicate phase-I (green), phase-II (red) and phase-III (orange).

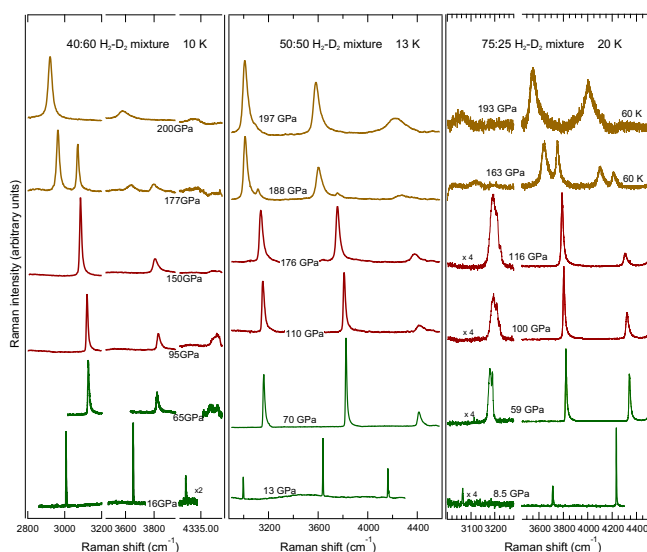


Fig. 4. Representative vibrational Raman spectra of 40:60, 50:50 and 75:25 H₂-D₂ mixtures as a function of pressure at 10 K, 13 K and 20 K respectively. Colours indicate phase-I (green), phase-II (red) and phase-III (orange).

and infrared frequencies in the pure isotopes, as shown in SI Appendix, Fig. S13. It also shows the comparison of Raman vibrational frequencies of H-H mode calculated in the ideal mixing of the alloy and measured in our experiment with different concentrations.

There is an interesting feature shared by all concentrations: rapid decrease of the H₂ vibron intensity as pressure is increased (see Fig. 4). While the vibrational modes attributed to D₂ and HD increase in intensity, the modes corresponding to hydrogen become significantly broader. This phenomenon was observed at room temperature and can be explained by H₂ being the lightest molecule and therefore it is scattered the most in collision with other molecules (1). Due to this effect, at pressures above 50-60 GPa, the overall appearance of the rotational/librational part of the Raman spectra is closer to pure D₂ (even for the 50:50 mixture at high pressures), while the spectra of the 40:60 mixture are almost indistinguishable from those of pure D₂ (Fig. 3 and Fig. 1 in Ref. (2)). As pressure is increased above 60-70 GPa the librational modes broaden and overlap significantly, making assignment difficult, with only the predominant S₀(0) modes in D₂ or H₂ clearly resolvable at around 200 cm⁻¹ at 65 GPa for the 40:60 mixture and around 360 cm⁻¹ at 76 GPa for the 75:25 mixture. Interestingly, the same modes are also relatively well defined in 50:50 mixture at 74 GPa even though the HD-S₀(0) was the predominant excitation at 29 GPa (Fig. 3, central panel).

When pressures above 100 GPa are reached, sharp low-frequency peaks emerge (see Fig. 3, see 95, 110 and 105 GPa) and the spectra of the 40:60 and 50:50 concentrations start to closely resemble those of pure D₂ in phase II (2), while the 75:25 spectra appear broadly similar to those of pure hydrogen (2) (see Fig. 3, and SI Appendix Figs. S6-S8). However, the transformation to phase II happens in the alloy at 69 GPa for 40:60, 75 GPa for 50:50, and 84 GPa for the 75:25 alloy (mixture) (see Fig. 1 and Fig. 3). The transformation pressures (at similar temperatures) to phase II depend on *ortho* – *para* ratio: for *n*-D₂ (*normal*-D₂, 2/3 *ortho* and 1/3

para mixed state) and *o*-D₂ vary from around 20 to 25 GPa (6, 24), from 60 to 110 GPa for *n*- and *p*-H₂ (2, 26), while for pure HD, the transformation pressure is around 60 GPa (21). The most unusual observation here is that even in the mixture (40:60), the Raman spectra look almost identical to those of pure D₂ (Fig. 3, left panel). However, the transition pressure to phase II is about 69 GPa, which is almost a 3-fold increase compared with pure D₂. In fact, the presence of hydrogen in the alloy pushes the phase II boundary of all concentrations close to that of pure *p*-H₂ at around 110 GPa (26).

The pressure needed to transform pure *para*-H₂ (sample was kept at 30 K for 72 hrs to achieve complete conversion) to phase II (~110 GPa) (26) is higher than that in the mixed *o*-*p* equilibrium state (~60 GPa) (on the time scale of our experiment ~3-5 hours) (2). This is primarily because the *ortho*-H₂ molecules in phase I are required by exchange symmetry to be in the *J* = 1 rotational state, this “trapped” kinetic energy makes them less stable than the ground *J* = 0 state adopted by *para*-H₂. One can expect the same destabilisation of phase I to apply to *para* D₂. However, because the excess energy of the *J* = 1 state is lower, and the *J* = 1 fraction at high-T is also lower (nuclear spin-state degeneracy of 3:6 rather than 3:1), the destabilisation of D₂ Phase-I is much smaller.

One might expect isotopic mixtures to be intermediate between H₂ and D₂, but in fact this scenario plays out in a more counterintuitive way at very low T when the *o*-*p* ratio is trapped at its room temperature equilibrium value. This is due to the effect we call “quantum trapping”*. Direct evidence of quantum trapping is clearly shown in Fig. 3 where the S(1) Raman transition (due to the trapped *J* = 1 states) is observed for H₂ or D₂, but absent for HD. To our knowledge, this is the only qualitative experimental signature of the exchange interaction. As seen in Fig. 3, the broken-symmetry phase II is characterised by non-rotor peaks around 150 cm⁻¹.

The trapped kinetic energy in *J* = 1 states increases the free energy of phase I. But since HD molecules have exchange symmetry, so at low temperature *all* HD molecules will be in the *J* = 0 ground state, so the trapped kinetic energy of phase I is lower in mixtures than in either pure element. Consequently, phase I survives to higher pressures in the molecular alloy. Of course, the zero-point effects are still smaller in HD than in H₂, so the HD transition still occurs at lower pressure than in *para*-H₂. The exact position of the transition will depend both on the H:D concentration and the *o* : *p* ratio.

Fig. 4 shows isotope effects in the transition to phase III: mixtures transform at higher pressures than the pure species. The transition to phase III is characterised by the splitting of the ν_1 modes, identical to that observed in the pure isotopes. As with the phase I-II transition, the mixtures are behaving like a molecular alloy, with all peaks splitting simultaneously from phase II to phase III. At low temperatures (around 20 K) the II to III phase transition starts at approximately 160, 159 and 165 GPa (2, 21) for pure H₂, HD and D₂ respectively, while phase III occurs at 177 GPa, 185 GPa and 171 GPa for the 40:60, 50:50 and 75:25 alloys (Fig. 4). Similar to the pure isotopes, all 3 mixture concentrations have phase co-existence regimes of approx. 10-15 GPa.

The phase II-III transition occurs at pressures where the vibron frequency is significantly decreasing, presumably associated with increased bondlength and the molecule becoming

*details of the *para* and *ortho* states and corresponding statistics are given in the SoM

more elliptical. Thus packing efficiency of three-dimensional ellipsoids can be taken as the driving force for the transition (13). The electric dipole of HD is so small that dipole-dipole interactions contribute only μeV of energy. It is well known that poly-dispersity reduces the packing efficiency, so the thermodynamic density "advantage" of phase III is lower in mixtures, meaning that higher pressures are required to stabilise it.

By combining all the P - T paths taken for the different concentrations, we are able to constrain the phase diagram of the H-D molecular alloys (Fig. 1) with $o-p$ ratios characteristic of rapid cooling. Although the overall phase diagram(s) resemble the pure isotopes there are some interesting and unusual features. All the phase I-II transition pressures in mixtures of all concentrations are higher than those of pure isotopes. Logically, the phase boundaries of the mixtures is consistent with that of the predominant isotope *i.e.* the 40:60 mixture boundary is at lowest pressure which is closest to that of pure D_2 among these three concentration mixtures, while 75:25 mixture boundary is at highest pressure which closest to that of pure H_2 among these three concentration mixtures. We note here that the Raman spectra in phase II could also be described as either "hydrogen-like", having features similar to pure hydrogen (see Fig. 3 and SI Appendix Fig. S11, 75:25 mixture) or "deuterium-like", having features similar to pure deuterium (see Fig. 3, and SI Appendix Fig. S11, 40:60 mixture and 50:50 mixture).

Surprisingly, the mixtures' phase II-III transition boundaries do not lie between those of hydrogen and deuterium as one would expect, but are shifted to higher pressures starting the transition at 163 GPa and completed by 191 GPa (see SI Appendix, Fig. S12). Just like in case of phase I to phase II the doping stabilises the lower pressure phase (phase II in this case). It is interesting that phase II of the 50:50 molecular alloy appears to resist the transformation to phase III up to the highest pressures and covers a larger amount of P - T space.

We have also explored phase III-IV boundary in the molecular alloys. The Raman spectra of the 50:50 mixture collected over a broad region of phase III (see the P - T paths taken in inset to Fig. 1) indicate that phase III is stable up to 260 GPa in a broad temperature range, transforming to phase IV at temperatures above ~ 250 K. A recent IR study (22) showed that above 160 GPa, pure HD dissociates and recombines forming a molecular mixture of H_2 , HD and D_2 similar to the 50:50 mixture studied here. It was then claimed that this mixture forms two novel phases, above 200 GPa, IV* and HD-PRE, both of which occupy phase space that we attribute to phase III (see phase lines on Fig. 1 inset). Our current study, and a previous room temperature study (1), suggests that the overall appearance of the phase diagrams of the molecular alloys is similar to those of the pure elements. Ref. (22) presented only one experimental run, without any raw data present, making it unclear what exactly their transition criteria to these phases are. It is also peculiar that these transition lines do not resemble anything observed in the pure isotopes H_2 and D_2 . Therefore, it is highly unlikely that the H:D mixture would have 2 solid phases never observed in pure hydrogen and deuterium.

The strong $S(1)$ peaks seen after rapid cooling prove that the nuclear spin state is trapped. In the case of H_2 and D_2 , the constraints from exchange symmetry mean some molecules are trapped in the high energy $J = 1$ rotational state in Phase I.

This extra rotational energy destabilises Phase I with respect to Phase II, causing the transition to occur at lower pressures than in HD-containing mixtures. This quantum trapping of rotational energy has the effect of moving the phase boundaries in a reproducible manner.

Methods. Samples of H_2 - D_2 mixtures were produced by combining research grade (99.999% purity) H_2 and D_2 in the gas phase (typically < 10 MPa) at 300 K. The partial pressures of each species were then used to calculate the compositions. Immediately after loading at 0.2 GPa, the Raman modes of H_2 and D_2 are clearly observed while the Raman mode corresponding to HD is weak, suggesting the dissociation and recombination of the molecules at this density is kinetically slow. Upon further compression in the fluid state (> 0.5 GPa), HD begins to rapidly form, evident through the H-D vibrational mode which grows with intensity with time until equilibrium is reached between H_2 , HD and D_2 . After the equilibrium is reached the intensities of 3 vibrational modes in the fluid state correspond to the gas concentration (see SoM for more details and calculations) and do not change with time implying the reversibility of the reaction.

Raman spectroscopy measurements were made using a custom-built micro-focused Raman system (2). The excitation source was a 532 nm laser, and the laser power was between 10-50 mW, with collection times ranging between 3-30 s. For diamonds with culet size bigger than 100 μm and pressure below 50 GPa, pressure was measured using ruby spheres and correlated with the frequency of the stressed diamond edge. For diamond with culet size smaller than 100 μm or pressure above 50 GPa the stressed diamond edge was used to estimate the pressure using the relationship from Akahama *et al.* (27).

In the typical isothermal experiment the sample was cooled down within 1-2 hrs and then the Raman spectra were collected within 3-4 hours upon pressure increase. In the typical isobaric experiment the target pressure would be reached at 300 K, sample cooled within 1-2 hours and Raman spectra were measured upon warming. In our experiments the samples were not kept at very low temperatures (50 K $<$) for more than 5-6 hours (see Ref. (24) where normal hydrogen (deuterium) converted to the p - H_2 (o - D_2) after app. 3 days at below 50 K). For examples, the estimate of the intensities of the $S_0(0)$ and $S_0(1)$ at 0.5-1 GPa and 300 K gives expected *ortho-para* ratio of 3:1 for H_2 and 2:3 for D_2 . Upon cooling to 20 K, which usually takes around 3 hours, at pressures below 50 GPa the ratio hardly changes for H_2 . Therefore we consider our sample to be in the mixed *ortho-para* state. All data referred to in the manuscript are available in the article and in SI Appendix.

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